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ON EXPLOSIVE REACTIONS OF GASES. I.

Explosion Limits of Oxyhydrogen Gas.

By Shoji Kimata, Norimasa Aomi and
Rempei Gotô.

Introduction.

With respect to the thermal explosion of a mixture of an inflammable gas and oxygen or the air in a closed vessel, it is well known that there exist two pressure limits—upper and lower—within which alone the explosion takes place. According to Hinshelwood[1], Semenoff[2] and other investigators, the lower limits is affected by the property of the surface of the reaction vessel used, and is lowered by the enlargement of the diameter of the vessel and also by introducing an inert gas so that the explosion takes place more easily. The upper limit is affected neither by the property of the surface nor by the size of the diameter of the vessel, but it is lowered by introducing an inert gas which makes the explosion harder to break out. These facts have been explained by the assumptions that (1) the gas explosion is mainly a chain reaction in the gaseous phase, (2) the chain breaks on the wall of the vessel at lower pressures, and (3) at higher pressures it is broken by a triple collision in the gaseous phase. The thus proposed chain theory of explosive reactions of gases premises the fact that the upper pressure limit chiefly belongs to the process in the gaseous phase and is almost independent of the surface of the reaction vessel. However, an careful examination of the experimental results obtained by Hinshelwood and other investigators exposes tolerably abundant facts which leave the doubt that the upper limit bears a close relationship to the surface of the vessel. For example, the upper limit curve obtained by Hinshelwood[3] shows clearly the effect of the surface. It is to be noted that in an aluminum or silver vessel[5] low pressure explosion is so much retarded that no limit curve can be obtained. Poljakow[6] pointed out that platinum wire (0.2 m.m. thick) placed in a silica tube exerts a retarding action on explo-

1) Hinshelwood and Williamson, "*The Reaction between Hydrogen and Oxygen.*" Oxford (1934).
2) Semenoff, "*Chemical Kinetics and Chain Reactions.*" Oxford (1935).
3) Thompson and Hinshelwood, *Proc. Roy. Soc.*, 122, 610 (1929).
4) Garstang and Hinshelwood, *ibid.*, 130, 640 (1930).
5) Hinshelwood, Moelwyn-Hughes and Rolfe, *ibid.*, 139, 521 (1931).
6) Poljakow and Neumark, *Acta Physicochim.*, 9, 163 (1938).

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sion, e.g. platinum wire which is more than 15 m.m. long makes the explosion peninsula vanish completely. According to him, platinum wire possesses not only an activity of generating the active centres which bring forth the chain reaction, but also that of breaking other active centres colliding with them, so that long platinum wire retards the chain reaction.

That the surface of a solid is of importance to explosive reactions of gases has been pointed out Haber and Alyea[7], and thus it has been admitted that the generation of the active centres has its origin in the surface of a solid. On the contrary, the part to be taken by the surface concerning the upper limit has been denied by Hinshelwood[8], Semenoff[9] and others. Nevertheless, this problem is not to be considered as decisively solved and it is still a most important point in the consideration of the mechanisms of explosive reactions. The authors have undertaken to ascertain the experimental factors taking part in the determination of the limits, especially the upper limit, of an explosive reaction between hydrogen and oxygen.

Experimental.

Apparatus and experimental procedure.

For the reaction vessels were used 6 kinds of pyrex tubes, as shown in Table I.

Table I.

	Length	Diameter	Internal surface area	Volume
No. 1	15 cm	4.0 cm	215 cm^2	19 cm^3
No. 2	"	3.2	164	117
No. 3	"	2.7	135	83
No. 4	"	2.1	102	51
No. 5	"	1.7	86	36
No. 6	"	1.3	64	20

These tubes were well rinsed with the bichromate-mixture and distilled water. In the examination of the effects of various salts the tubes were rinsed with dilute solutions of those salts and dried. In the examination of the effect of the vapour of

7) Haber and Alyea, *Z. physik. Chem.*, B 10, 193 (1930); Alyea, *J. Amer. Chem. Soc.*, 53, 1324 (1931).

8) Hinshelwood, *Trans. Farad. Soc.*, 28, 184 (1932).

9) Semenoff, *ibid.*, 29, 606 (1933); Lavrov and Bestchastny, *Acta Physicochim.*, I, 975 (1935).

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the salts a side tube containing the salts was attached to the reaction vessel and heated to the same temperature as the reaction vessel.

The observation of the upper limit was made mainly by the withdrawal method: Namely, (1) introducing the gas mixture at low temperatures, (2) heating it up and (3) withdrawing it. The explosive reaction was recognized by the discontinuous pressure decrease (pressure kick) indicated by a mercury manometer connected with the reaction vessel. The electrolytic gas ($H_2 : O_2 = 2 : 1$) was used in the experiment.

Results.

Experiment I. The general characteristics of the upper limit.

It has been admitted that the upper limit depends only on the temperature, the composition of the gases and the pressure. By the present experiment, however, it was ascertained that it is fundamentally affected by the experimental procedure.

a) Pretreatment of the reaction vessel.

The reaction vessel was evacuated for more than 30 minutes at 550°C. before use. When this pretreatment was made for a shorter time and at a lower temperature, the curve of the upper limit becomes generally low and irregular.

b) The velocity of the temperature rise.

The reacting gases are introduced into the pretreated reaction vessel heated to about 400°C. and then heated to the explosion temperature at the rate of 10°C. per minute. This velocity of the temperature rise exerts a remarkable influence on the upper limit: when the velocity of the temperature rise is large, the upper limit becomes high.

c) The velocity of the pressure decrease.

After the temperature has reached a definite point, the upper limit is reached by slowly decreasing the pressure at the rate of 1 m.m. per second. When the velocity of the pressure decrease is small, the upper limit tends to become low.

d) The size of the reaction vessel.

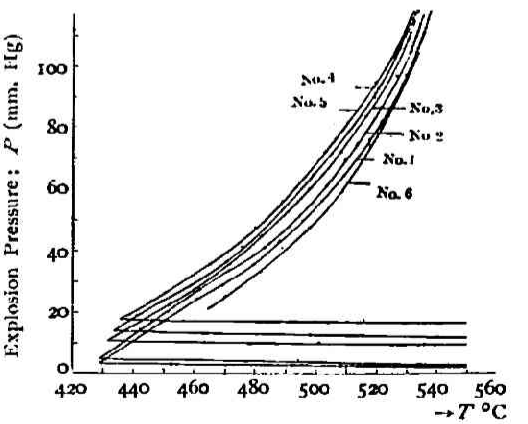

Fig. 1. Reaction tube No. 1, d=4.02 cm.; No. 2, d=3.15 cm.; No. 3, d=2.65 cm.; No. 4, d=2.07 cm.; No. 5, d=1.73 cm.; No. 6, d=1.30 cm.

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The upper limits observed by using various kinds of the reaction tubes, under such conditions as the rate of 10° per minute for the temperature rise and 1 m.m. per second for the pressure decrease are shown in Fig. 1.

As seen from this figure, the upper limit generally rises as the diameter of the reaction tube becomes smaller. When, however, the diameter of 1.3 cm. is reached, the upper limit lowers. Above 540°C. the same upper limit tends to be reached in all the reaction vessels. On the other hand, the lower limit gets lower with the increase of the size of the reaction vessel. In short, the explosion peninsula is generally lowered according as the size of the reaction vessel increases and the position of the critical point of explosion (the apex of the peninsula) lags towards the direction of the lower pressure and the lower temperature.

Experiment 2. Influence of various metals upon the explosion limit.

The results obtained by Poljakow[6] and Hinshelwood[5] suggest that the presence of metals shortens the explosion region. The present authors examined the influence of various metals upon the explosion limit. The experimental method was the same as noted in the previous section, namely, the explosion limits were observed by using various kinds of metal wires polished with emery paper and kept in the reaction vessel.

Generally speaking, in the presence of metals, when the temperature of the oxygen—hydrogen mixture is raised, the pressure is first found to increase slightly and then at a certain temperature it begins distinctly to decrease. If the temperature alone is further raised, explosion does not take place. When a certain temperature is attained, however, the withdrawal of the gas leads to explosion, thus making the measurement of the upper limit possible. Fig. 2 shows the effect of platinum wire observed by using the reaction vessel No. 1.

In the case of the reaction vessel containing platinum wire the upper limits is lowered and the lower limit raised as compared with the case of an empty vessel. The longer the platinum wire used is, the greater the effect is, and a platinum wire more than 10 m.m. long makes the explosion peninsula disappear completely. The effects of silver, nickel and aluminum are shown in Figs. 3, 4 and 5.

Thus, the following facts were experimentally confirmed: (1) the presence of metal wires lowers the upper limit; (2) the larger the surface area of the wire is the greater its effect is; (3) the total pressure decreases before starting of explosion in every case; (4) silver and nickel lose their lustre and activity as they are used; and (5) platinum produces the most remarkable effect and aluminium the least. The

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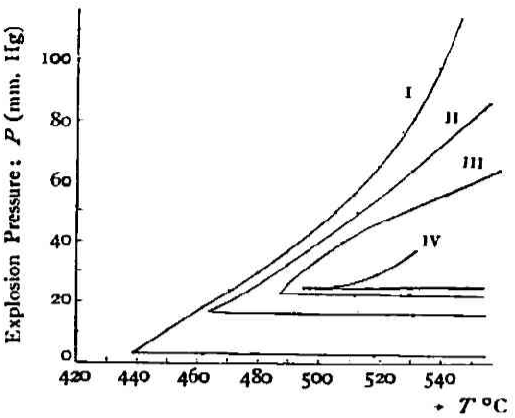

Fig. 2. Curve I, Empty; Curve II, Pt wire (0.2 ×1 mm.); Curve III, Pt wire (0.2×5 mm.); Curve IV, Pt wire (0.2×10 mm.). (Tube No. 1.)

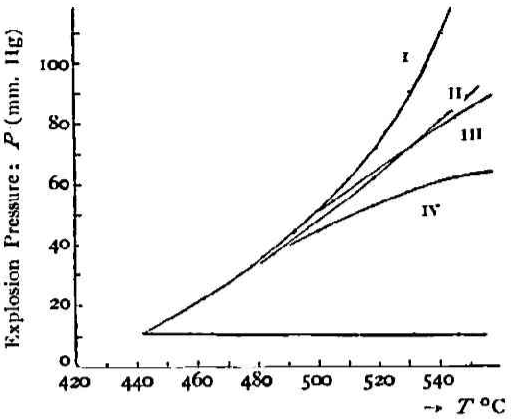

Fig. 3. Curve I, Empty; Curve II, Ag (0.25×5 mm.); Curve III, Ag (0.25×10 mm.); Curve IV, Ag (0.25×60 mm.). (Tube No. 3.)

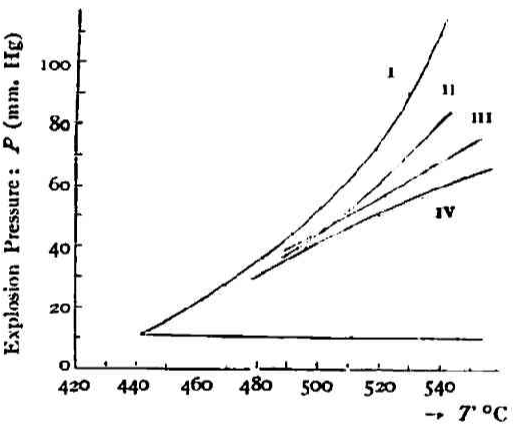

Fig. 4. Curve I, Empty; Curve II, Ni (0.25×5 mm.); Curve III, Ni (0.25×10 mm.); Curve IV, Ni (0.25×50 mm.). (Tube No. 3.)

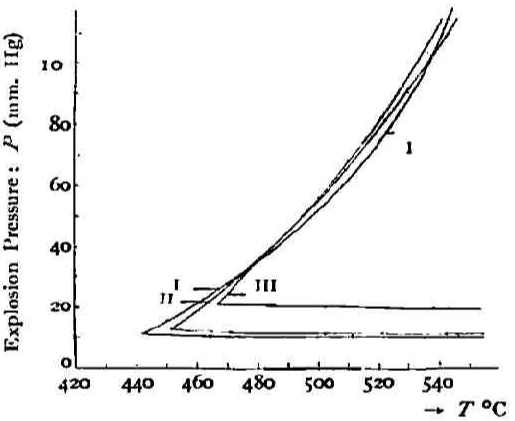

Fig. 5. Curve I, Empty; Curve II, Al rod (2.2 ×10 mm.); Curve III, Al rod (2.2×30 mm.). (Tube No. 3.)

decrease in the total pressure suggests that catalytic reactions are occurring on the surfaces of those metals. In other words, this explosive phenomenon belongs to the system containing the vapour of H_2O generated by the catalytic reaction of a metal. Accordingly, it is inferred that the effect on the upper limit is produced not directly by the surface of a metal, as Poljakow has assumed, but secondarily by the water vapour generated. In confirmation of this inference the effect of the water vapour was examined.

Experiment 3. The effect of the water vapour.

How is the curve of the pressure limit varied by adding the water vapour to an oxygen-hydrogen mixture at different rates? The experiments were carried out

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in the same way as Exp. 2 and the results observed are shown in Fig. 6. The presence of the water vapour lowers the upper limit and raises the lower limit. Accordingly, the above mentioned effect regarded as produced by a metal is to be considered as the effect of the water vapour. The fact that the effects of the metals become smaller at lower temperatures and lower pressures may be ascribed to the smallness of the amount of the water vapour present, judging from the lapse of time. The retarding action of the water vapour fluctuates according to the order of mixing. For example, when the water vapour is first introduced and then an oxygen-hydrogen mixture, the reaction is retarded more markedly than when an oxygen-hydrogen mixture containing the water vapour is introduced. And more than 5 m.m. of the water vapour retards the explosive reaction completely and slow reaction proceeds markedly.

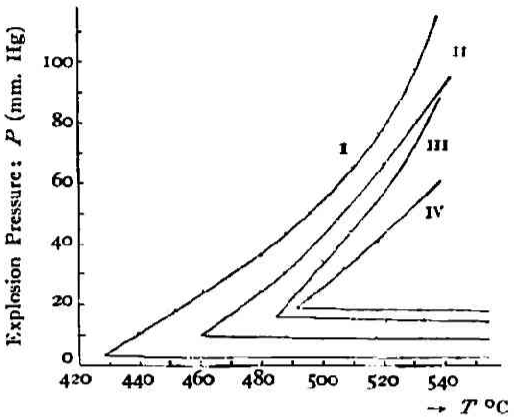

Fig. 6. Curve I, No vapour; Curve II, 1 mm. Hg H_2O; Curve III, 2 mm. Hg. H_2O; Curve IV, 4 mm. Hg. H_2O. (Tube No. 1.)

Experiment 4. Influence of various salts.

Pease[10] reported that the rate of reaction of an oxygen-hydrogen mixture passing through a pyrex tube at 520~550°C. at atmospheric pressure was very sensitive to the pretreatment of the surface. With the surface rinsed with a dilute potassium chloride solution, the yield of hydrogen peroxide was remarkably small and the temperature of explosion was high as compared with the surface rinsed with nitric acid and distilled water. This fact found by Pease was applied to the retardation of the surface reaction between hydrogen and oxygen by Alyea[11] and Oldenberg[12]. And it seems to indicate the presence of the effect of various salts on the explosion limit. The present authors observed the influence of salts in the following two ways.

1) Influence of the vapour of salts.

By heating various salts put in the side tube of the reaction vessel together with an explosion gas mixture, the explosion limit was observed. The results

10) Pease, *J. Amer. Chem. Soc.*, **52**, 5106 (1936).
11) Alyea, *ibid.*, **55**, 3227 (1933).
12) Oldenberg and Sommers, *J. Chem. Phys.*, **8**, 468 (1940); **9**, 115 (1941).

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obtained are shown in Figs. 7, 8 and 9. The lowering of the upper limits at 500°C. is tabulated in Table II. (The standard curve was drawn from Fig. 1 and, strictly speaking, it is subject to a more or less variation according to the nature of the surface.)

With potassium iodide, cobalt chloride and nickel chloride, the explosive reaction was so completely retarded that the explosion limit could not be observed. With nickel chloride, slow decrease of pressure was observed above 300°C.

Table II.

Salts	LiCl	NaCl	KCl	$CaCl_2$	$BaCl_2$	$AlCl_3$	NaBr	KBr	Na_2CO_3
Lowering of upper limit (m.m.)	18	0	5	11	−5	28	15	12	12

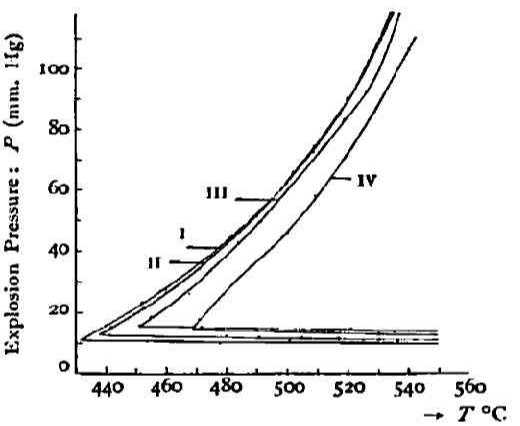

Fig. 7. Curve I, No vapour; Curve II, NaCl; Curve III, KCl; Curve IV, LiCl. (Tube No. 3.)

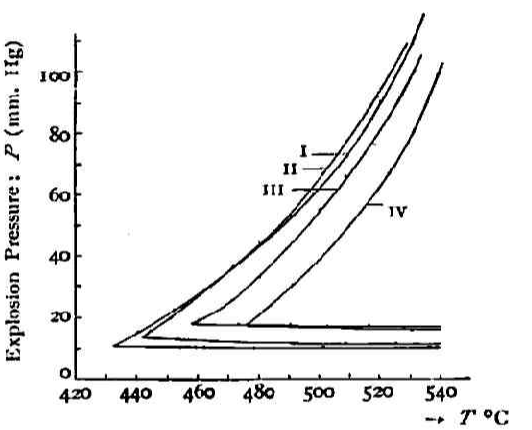

Fig. 8. Curve I, No vapour; Curve II, $BaCl_2$; Curve III, $CaCl_2$; Curve IV, $AlCl_3$. (Tube No. 3.)

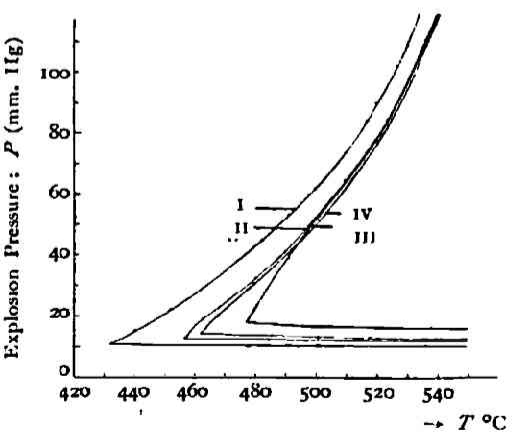

Fig. 9. Curve I, No vapour; Curve II, KBr; Curve III, Na_2CO_3; Curve IV, NaBr. (Tube No. 3.)

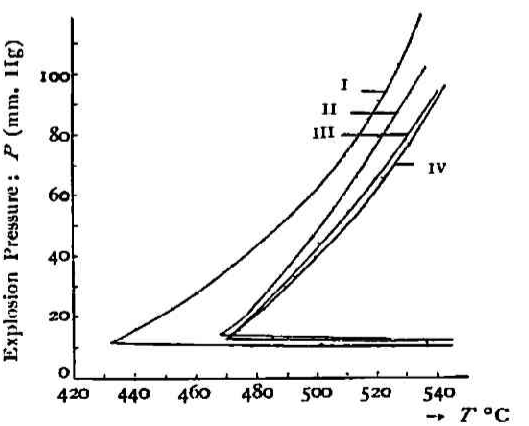

Fig. 10. Curve I, No treatment; Curve II, $\frac{1}{100}$ M NaCl solution; Curve III, $\frac{1}{10}$ M NaCl solution; Curve IV, 1 M NaCl solution.

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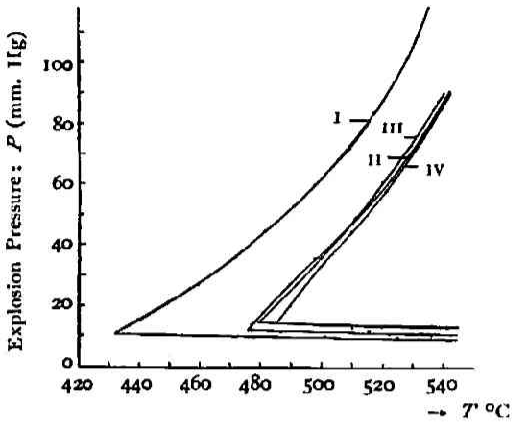

Fig. 11. Curve I, No treatment; Curve II, $\frac{1}{100}$ M KCl solution; Curve III, $\frac{1}{10}$ M KCl solution; Curve IV, 1 M KCl solution.

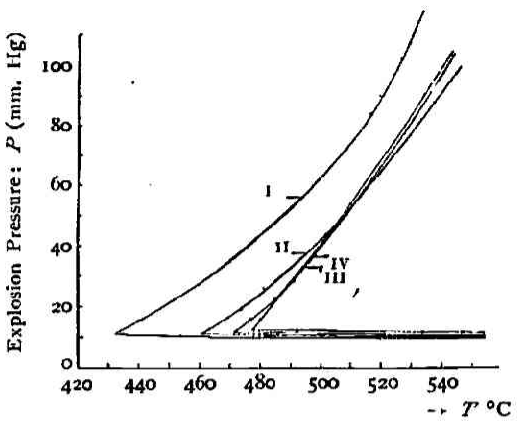

Fig. 12. Curve I, No treatment; Curve II, $\frac{1}{100}$ M $BaCl_2$ solution; Curve III, $\frac{1}{10}$ M $BaCl_2$ solution; Curve IV, 1 M $BaCl_2$ solution.

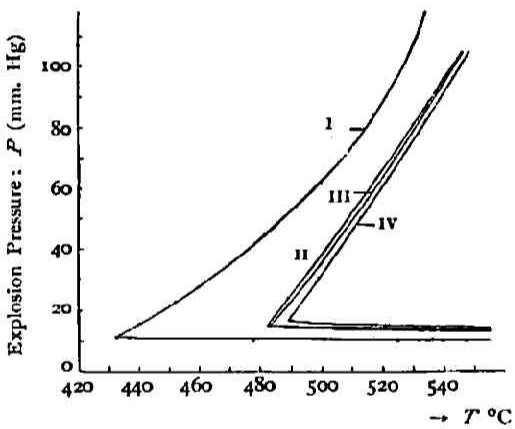

Fig. 13. Curve I, No treatment; Curve II, $\frac{1}{100}$ M $CaCl_2$ solution; Curve III, $\frac{1}{10}$ M $CaCl_2$ solution; Curve IV, 1 M $CaCl_2$ solution.

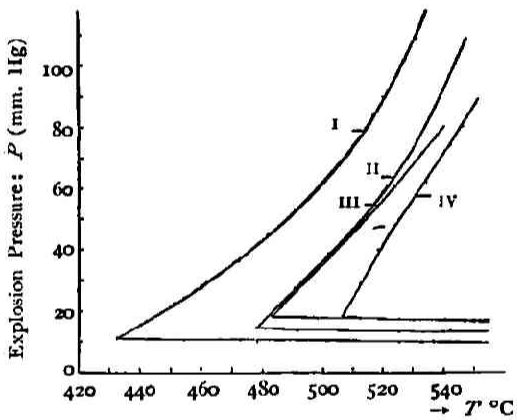

Fig. 14. Curve I, No treatment; Curve II, $\frac{1}{1000}$ M KI solution; Curve III, $\frac{1}{10}$ M LiCl solution; Curve IV, $\frac{1}{100}$ M $NiCl_2$ solution. (Tube No. 3.)

2) Influence of the surface treatment with salt solution.

By using the reaction vessel the inner wall of which was rinsed with dilute solutions of various salts, the explosion limit was observed. The results obtained are shown in Figs. 10, 11, 12, 13, and 14, and the lowering of the upper limit at 500°C. is compared in Tables III and IV. These results show that the influence of the surface treatment is greater than that of the vapourof the salts. The influence of concentration is generally small at more than 1/100 M. With potassium iodide and nickel chloride, the concentration greater than 1/10 M retards the explosion reaction.

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Table III.

	NaCl (Fig. 10)			KCl (Fig. 11)			$BaCl_2$ (Fig. 12)		
	$\frac{1}{100}$ M	$\frac{1}{10}$ M	1 M	$\frac{1}{100}$ M	$\frac{1}{10}$ M	1 M	$\frac{1}{100}$ M	$\frac{1}{10}$ M	1 M
Lowering of upper limit (m.m.)	14	19	25	26	23	28	22	20	23

Table IV.

	$CaCl_2$ (Fig. 13)			KI	LiCl	$NiCl_2$ (Fig. 10)
	$\frac{1}{100}$ M	$\frac{1}{10}$ M	1 M	$\frac{1}{1000}$ M	$\frac{1}{10}$ M	$\frac{1}{100}$ M
Lowering of upper limit (m.m.)	24	27	31	26	27	50 (507°C)

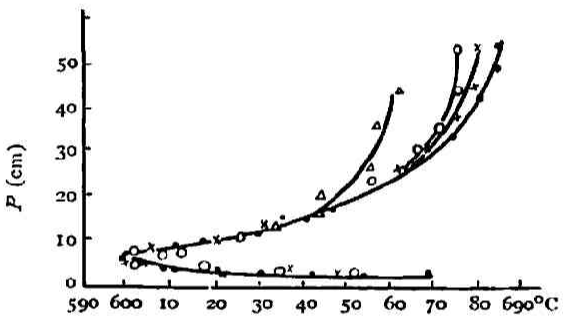

Fig. 15. Influence of stream velocity on region of inflammation of $2CO+O_2$. (Sagulin.)

Discussion.

It has been admitted that the upper pressure limit of explosion depends only on the constitution of the gas, the pressure and the temperature. However, the above-mentioned experimental results prove that it also depends on other factors. Each factor will be discussed below.

Experiment 1.

1) Remarkable influence of the pretreatment of the surface on the upper limit shows that there holds a close relationship between the performance of such an explosive reaction and the surface condition. In the case of incomplete preliminary evacuation something which remains on the surface—probably the water vapour—seems to retard the explosive reaction.

2) The influence of the velocity of heating on the upper limit is connected with the duration of the time when a mixture is kept at high temperatures with-

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out exploding. It is expected that the duration of the time allows a slow catalytic reaction to proceed on the glass surface. Although a measurable decrease of the pressure is not observed when the heating velocity is small, yet the existence of the same surface condition is conceivable as in the case of incomplete preliminary evacuation. When the duration of heating is long, the water vapour catalytically generated may enough retard explosion.

3) The influence of the velocity of withdrawing can be discussed from the two different stand-points—(1) the above noted duration of slow reaction and (2) the turbulence of the gas by the withdrawing procedure. It is probable that the withdrawing procedure produces the effect similar to the streaming method. But, according to the experimental results of Semenoff[13] and others obtained by the streaming method, the larger the streaming velocity is, the more widely the explosion region extends (the cause of this phenomenon has not been explained). Both streaming and withdrawing are regarded as the washing effect, so that they are considered to have the probability of accelerating the surface reaction.

4) Hinshelwood maintains from his experimental results that the diameter of the reaction vessel has no relation to the upper limit. The results obtained by the present authors, however, are quite the reverse. Though the cause of this discrepancy is not clear, it seems to be due to the variation in the said washing effect caused by the size of the reaction vessel. Anyhow, so long as the explosive phenomenon is regarded as a simple homogeneous gaseous reaction, it will be impossible to explain the above decribed facts, (1) (2) (3) and (4).

Experiment 2.

Experiment 2 shows that various metals retard the explosive reaction, as Poljakow has pointed out. Poljakow assumes that this retarding effect of metal is due to the breaking of the active centres by colliding with the metal surface. Similarily, Hinshelwood[14] explained the fact that the explosion peninsula disappears in the case of a silver vessel. On the other hand, Lewis[15] proposed the hypothesis that the retarding effect in the case of a silver vessel is due to the break of the chain caused by the action of silver or some silver compound in a vapour form. In this case, it is to be noted that the water vapour generated by the catalytic effect of silver or other metals coexists. And the coexisting water

13) Sagulin, Kowalsky, Kopp and Semenoff, *Z. physik. Chem.*, B, 6, 307 (1930).

14) Hinshelwood, Moelwyn-Hughes and Rolfe, *Proc. Roy. Soc.*, 139, 521 (1933).

15) B. Lewis and G. von Elbe, "*Combustion, Flame and Explosions of Gases*"; H. Heiple and B. Lewis, *J. Chem. Phys.*, 9, 120 (1941).

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vapour can retard the explosion reaction, as clearly shown in Experiment 3. Therefore, it is appropriate to consider that explosion is retarded not by a metal itself but by the water vapour secondarily generated. Apparently there is much difference in nature between the effect of a metal and that of the water vapour, but it will be explainable by taking into account the fact that when the temperature gets higher, the steam content increases in volume.

The retarding effect of salts in Experiment 4 is markedly different from that of metals except nickel chloride. In the case of salt the pressure decrease was not observed even when a striking retarding effect is produced. Namely, the catalytic power of salt seems weaker than that of metal. The retarding effect, therefore, in this case is not considered to be due to the water vapour secondarily generated. According to Pease, salt is to retard the catalytic reaction on the glass surface.

In the case of nickel chloride, the pressure decrease is clearly observed just as in that of metal, so that the effect seems to have been produced by the water vapour catalytically generated. It is uncertain whether remarkable retarding action of nickel chloride or potassium iodide is exerted by the salts themselves or by a substance formed by their decomposition. And it is also uncertain whether the retardation by the water vapour and salt occurs in the gaseous phase or on the wall of the reaction vessel. Judging from a striking influence of the surface treatment, it is inferred that it occurs on the surface. If this inference is correct, the explosive reaction at the upper limit is not the process in the gaseous phase as hitherto admitted, but the surface phenomenon. This problem will be discussed later.

Summary.

1) It has been found that the upper explosion limit is varied by the experimental procedures and conditions, such as (i) the pretreatment of the reaction vessel, (ii) the velocity of heating (iii) withdrawing, and (iv) the diameter of the vessel.

2) The retarding effects upon explosion of various metals, salts and the water vapour have been observed.

3) It is inferred that the effect of metal is due to the water vapour generated by its catalytic action.

4) It is also inferred that the retarding effect of salts is produced on the surface of the vessel.

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